

AD-A286 562

ENTATION PAGE

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Form Approved
OASD No. 0704-0188

Intended to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

PORT DATE October 31, 1994 13. REPORT TYPE AND DATES COVERED Final 4/91-8/94

4. TITLE AND SUBTITLE

NOVEL REAGENTS FOR CHEMICAL VAPOR
DEPOSITION OF INTERMETALLIC ALLOYS

6. AUTHOR(S)

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5. FUNDING NUMBERS

2303-B2
61102F

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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360 Huntington Ave.
Boston, MA 021158. PERFORMING ORGANIZATION
REPORT NUMBER

AFOSR-TR- 94 0723

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NEU
Building 410, Bolling AFB
20332-6448
Dr. Hedberg10. SPONSORING/MONITORING
AGENCY REPORT NUMBER

AFOSR-91-0207

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for Public Release; Distribution is
unlimited

12b. DISTRIBUTION CODE

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13. ABSTRACT (Maximum 200 words)

Reactions of $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ with AlMe_3 proceed by formation of covalent
ly bonded heterobimetallic intermediates with no alkyl exchange. Reaction
with $\text{AlH}_3 \cdot \text{NMe}_3$ yielded $\text{Al}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{NMe}_3$ and " $\text{Hf}(\text{CH}_2\text{SiMe}_3)_3\text{H}_3$ ".
Carbon blocks coated with this mixture produced a HfAlC_2 coating which
was effective in protecting the substrate from air oxidation at high
temperatures.

DTIC QUALITY INSPECTED 5

14. SUBJECT TERMS

Molecular precursors, ternary metal/
aluminum carbides, oxidation protection, carbon comp-
osites.

15. NUMBER OF PAGES

19

16. PRICE CODE

17. SECURITY CLASSIFICATION
OF REPORT

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18. SECURITY CLASSIFICATION
OF THIS PAGE

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19. SECURITY CLASSIFICATION
OF ABSTRACT

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20. LIMITATION OF ABSTRACT

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FINAL PROJECT REPORT

TITLE: Novel Reagents for Chemical Vapor Deposition of Intermetallic Alloys

CONTRACT GRANT NUMBER: AFOSR-91-0207

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PUBLICATIONS:

"Alkyl for Hydride Exchange Between Alane-Trimethylamine and Group IVB Metal Alkyls

William G. Felghery, Rein U. Kirss, Charles H. Lake, and Melvyn Rowen Churchill, *Inorg.*

Chim. Acta, 1994, 218, 47-51.

"Reactions of Tetrakis(trimethylsilylmethyl)hafnium With Trimethylaluminum

Rein U. Kirss, William G. Felghery, and Douglas C. Gordon, *Inorg. Chim. Acta*, 1994, in

press

ABSTRACT:

Alkyl exchange reactions between group IVB transition metal alkyls (MR_4 where $M = Ti, Zr, Hf$ and $R = Me_3CCH_2, Me_3SiCH_2$) and aluminum alkyls (AlR_3 , where $R = Me, Et, H$) were studied by multinuclear NMR spectroscopy ($^1H, ^{13}C, ^{27}Al$). In the case of $Hf(CH_2SiMe_3)_4$ and $AlMe_3$, evidence for the formation of neutral bimetallic complexes was observed without the observation of alkyl exchange. Reactions between $Hf(CH_2SiMe_3)_4$ and $AlH_3 \cdot NMe_3$ yielded $Al(CH_2SiMe_3)_3 \cdot NMe_3$ and " $HfH(CH_2SiMe_3)_3$ ". The former was characterized by single crystal x-ray diffraction. In all other exchange reactions, decomposition was too rapid for the observation of alkyl exchange or intermediates. Pyrolysis of $Hf(CH_2SiMe_3)_4 / AlH_3 \cdot NMe_3$ mixtures yielded black powders which analyzed for " $HfAlC_2$ ". Carbon blocks were dip-coated with $Hf(CH_2SiMe_3)_4 / AlH_3 \cdot NMe_3$ mixtures and pyrolyzed to give an mixed metal oxide / metal carbide coatings which gave some measure of oxidation protection at 600°C.

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Introduction

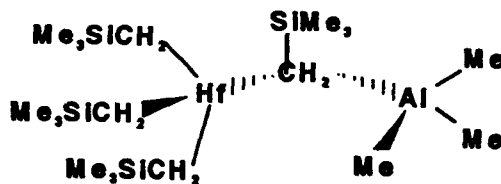
We have been investigating molecular precursors for the chemical vapor deposition of intermetallic alloys of aluminum and group IVB transition elements (Ti, Zr, and Hf) on carbon substrates as oxidation protection for the carbon materials. Our efforts have been concentrated in three areas:

1. investigations of the alkyl exchange reactions between group IVB and aluminum alkyls,
2. preparation and characterization of ternary aluminum/group IVB metal carbides from molecular precursors, and
3. evaluation of coatings prepared from molecular precursors in 2 with respect to oxidation protection of carbon blocks.

Further details of each of these projects is provided in the attached manuscripts/reprints.

Exchange Reactions

Reactions between TiMe_4 , Cp_2ZrMe_2 or $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and AlMe_3 were investigated using conductivity measurements and ^1H NMR spectroscopy. Little change was observed in the conductivity of $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4/\text{AlMe}_3$ or $\text{AlMe}_3/\text{Cp}_2\text{ZrMe}_2$ mixtures in dichloromethane relative to the molar conductivity of the reactants. In the presence of PEt_3 , a small increase in conductivity was observed for the latter solution. A fifty fold increase in the conductivity was observed in mixtures of TiMe_4 and AlMe_3 . Spectroscopic studies on mixtures of $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and AlMe_3 were consistent with formation of a thermally unstable, alkyl bridged heterobimetallic complex, 1, present in a 5:1 ratio to the starting materials. There was no evidence for alkyl exchange in these reactions.



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Reaction of equimolar amounts of $\text{AlH}_3 \cdot \text{NMe}_3$ and $\text{M}(\text{CH}_2\text{SiMe}_3)_4$ in benzene (for $\text{M} = \text{Zr}, \text{Hf}$) led to exchange of all three Al-H bonds for $\text{Al-CH}_2\text{SiMe}_3$ bonds and isolation of $\text{Al}(\text{CH}_2\text{SiMe}_3)_3 \cdot \text{NMe}_3$ (2).

The latter compound crystallized $P1$ space group, a 9.535(2), b 10.913(2), c 12.273(2) Å, α 88.03(1), β 86.03(1), γ 86.93(1)°, U 1271.6(4) Å³, D_c 1.002 g cm⁻³, $Z=2$, $\mu(\text{Mo-K}\alpha)$ 0.217 mm⁻¹, $F(000)=424$. Similar reactions between $\text{AlH}_3\cdot\text{NMe}_3$ and Cp_2ZrR_2 ($R = \text{CH}_3, \text{CH}_2\text{SiMe}_3$) yielded Cp_2ZrH_2 and $\text{AlR}_3\cdot\text{NMe}_3$. Reaction of $\text{AlH}_3\cdot\text{NMe}_3$ with $\text{Zr}(\text{CH}_2\text{Ph})_4$ produced $\text{Al}(\text{CH}_2\text{Ph})_3\cdot\text{NMe}_3$.

Preparation of Ternary Group IVB Aluminum Carbides From Molecular Precursors

Reaction of $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ or $\text{Zr}(\text{CH}_2\text{SiMe}_3)_4$ with one equivalent of $\text{AlH}_3\cdot\text{NMe}_3$ in solution, followed by evaporation of the solvent and pyrolysis of the residue under argon (850°C for 16 hours), yielded a black crystalline powder, impervious to all mineral acids and strong oxidizing solutions. Combustion analyses for C, H and N were consistent with a formulation as HfAlC_2 and $\text{ZrAlC}_{1.4}$. EDX analysis revealed the presence of both aluminum and hafnium in the HfAlC_2 product. Silicon was not detected in the latter measurements. The reaction of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_4$ with $\text{AlH}_3\cdot\text{NMe}_3$ at room temperature resulted in immediate decomposition without detection of any intermediates. Combustion analysis of the annealed products from reactions of $\text{Ti}(\text{CH}_2\text{SiMe}_3)_4/\text{AlH}_3\cdot\text{NMe}_3$ were consistent with the formulations $\text{TiAlC}_{1.2}$ based on retention of the initial 1:1 stoichiometry of the metals.

Evaluation of HfAlC_2 Coated Carbon Blocks In An Oxidative Environment

When solutions generated from $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and $\text{AlH}_3\cdot\text{NMe}_3$ were used to coat carbon blocks and annealed under argon, thin coatings of the HfAlC_2 phase were obtained. ESCA analysis (Table 1) of the coated blocks were consistent with a 1:1:2 stoichiometry for the three elements, respectively, however, large amounts of oxygen, most likely in the form of metal oxides was also observed. The most likely source of metal oxides is believed to be the result of atmospheric oxygen introduced during the annealing process through small leaks in the system combined with high annealing temperatures and long annealing times. This conclusion is supported by the nearly constant or slightly increasing concentrations of aluminum and hafnium as a function of depth while the oxygen concentration decreases steadily when sputtered below the surface layer. The formation of metal oxides is not necessarily a major problem for coatings applications, as air oxidation of the metal carbide coating to metal

oxides is anticipated to be the mechanism for protection of the substrate. Alumina in particular has been investigated as oxidation resistant coatings for carbon based materials. Powder diffraction experiments on the coated blocks reveal a single major peak likely to correspond to diffraction by the carbon substrate. Smaller, broader peaks were too weak in intensity to identify the nature of the coating (Figure 1).

Table 1: ESCA Analysis Of T300 Carbon Blocks Coated From $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$

Coating Solution	Depth (Å)	$\text{HfAlH}_3\cdot\text{NMe}_3$ Mixtures		Atom %		
		Hf	Al	Si	C	O
single coat from hexane solution	surface	11.3	25.0	5.2	31.2	27.3
	20	11.9	26.3	4.7	28.1	29.0
	3000	8.8	5.8	0	72.4	13.0
triple coat from benzene solution	surface	4.4	9.2	6.4	42.5	37.5
	20	5.8	9.1	5.7	39.4	40.0
	320	6.9	6.2	3.4	58.7	24.8

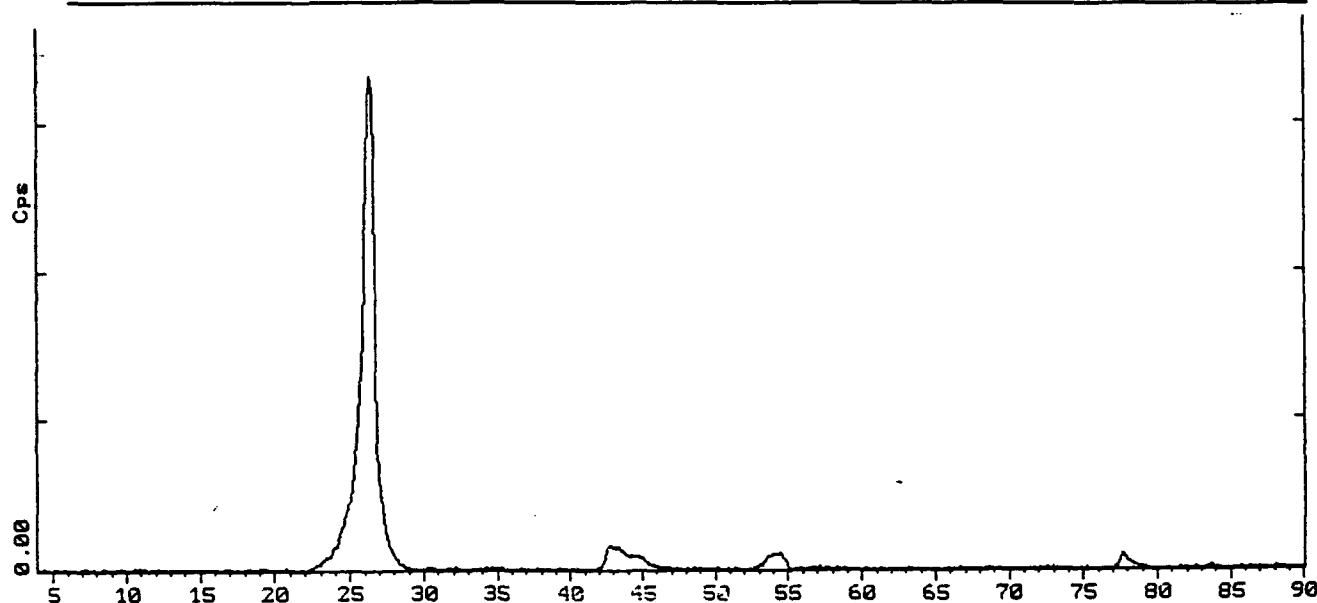


Figure 1: X-ray Powder Diffraction Pattern of T300 Block Coated With HfAlC_2

The oxidation behavior of carbon blocks coated with a single layer of mixed metal carbides from $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4 / \text{AlH}_3\cdot\text{NMe}_3$ mixtures coated blocks was evaluated by pyrolysis in air at 600°C and 900°C with the results summarized in Table 2. The data show that the HfAlC_2 coating acts to protect the underlying carbon substrate for short periods, although the degree of protection from this single coating is understandably far from optimal. The 41% ceramic yield of HfAlC_2 from mixtures of $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and $\text{AlH}_3\cdot\text{NMe}_3$ was expected to produce cracks and pinholes in the coating exposing the underlying carbon

substrate to air oxidation. The concentration of the coating solution has a measurable effect on the oxidation behavior of the blocks. The highest concentrations appear to leave thicker coatings more susceptible to cracking as observed by SEM. Very dilute solutions provide for inadequate surface coverage, exposing the substrate to rapid air oxidation. Coatings prepared from benzene solutions of $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and AlH_3NMe_3 were observed to be superior than coatings prepared in hexane solution.

Table 2: Oxidation Protection of T300 Carbon Blocks By A Single Coat of HfAlCl_2

Concentration of Coating Solution	% Weight Loss after 4 hours at	
	600°C	900°C
Uncoated T300	28.5	85.5
1.0 M	21.4	61.6
0.1 M	16.6	32.6
0.05 M	11.5	35.6
0.01 M	13.3	85.3

The effect of multiple coatings on the oxidation behavior of carbon blocks are summarized in Table 3. The multiple coated blocks were prepared at a constant concentration of 0.1 M for the coating solution by repetition of the coating and annealing cycles as described above for the single coated blocks.

Table 3: Oxidation Protection of T300 Carbon Blocks By Multiple Coats Of HfAlCl_2

Number of Coating Annealing Cycles	% Weight Loss		
	600°C/4 h	600°C/10 h	900°C
1	12.0	40.2	
2	15.9	40.7	35.6
3	16.92	29.0	

As expected, the rate of oxidation increases with temperature. The rate of oxidation (Figures 2-4) for the different number of coatings appears to be qualitatively the same for the single, double and triple coated blocks, suggesting that 1) multiple coatings are unable to fill the space left by the initial coating (i. e. pinholes, cracks are of molecular dimensions) or 2) the coating materials themselves are chemically modified and either consumed or detached from the block exposing the carbon substrate to air oxidation. Prolonged oxidation of a triple coated block at 900°C (8 hours) leads to complete consumption of the carbon block leaving a residual white crystalline powder identified by x-ray diffraction as HfO_2 (Figure 5).

Data from "344-18-1"

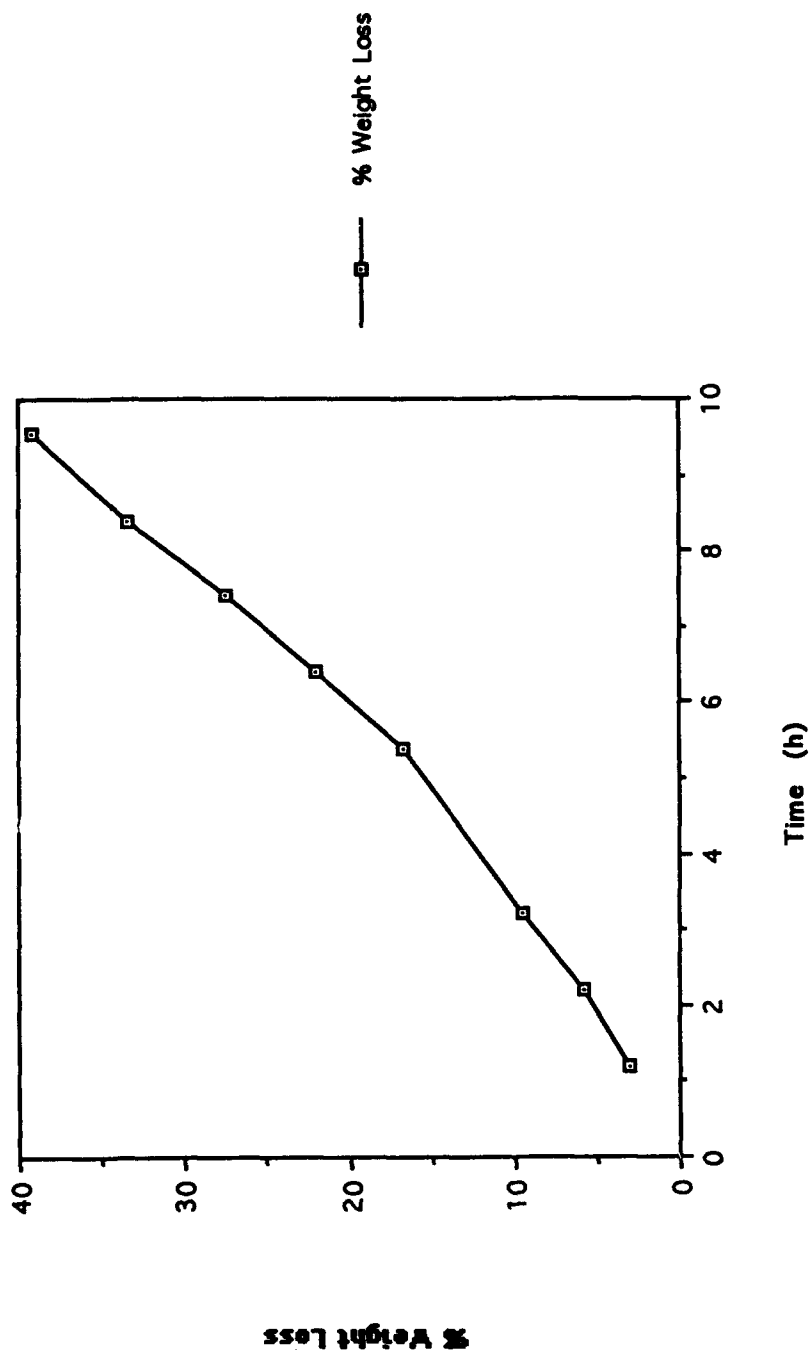


Figure 2: Oxidation Rates of Single Coated T300 Block

SEPTEMBER 02, 1994
"Pyrolysis of 344-18-2(Double coated block)"

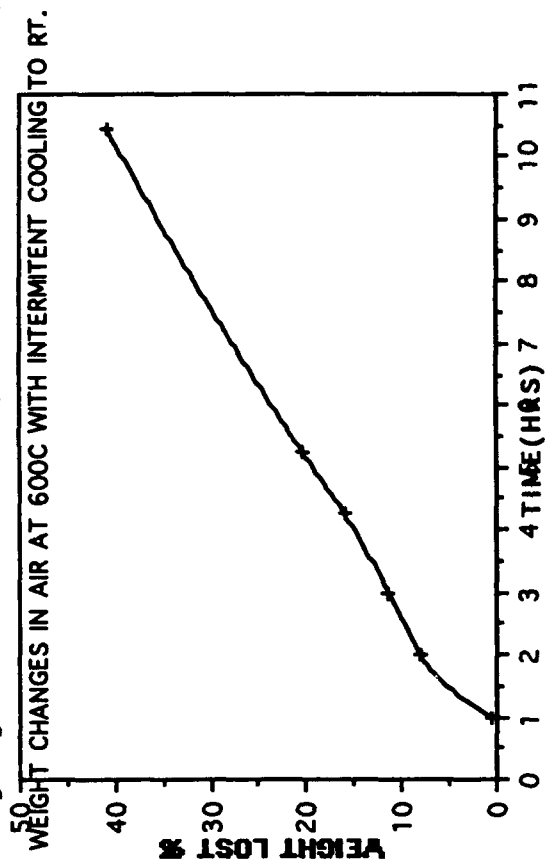


Figure 3: Oxidation Rates of Double Coated T300 Blocks

Data from "344-18-3"

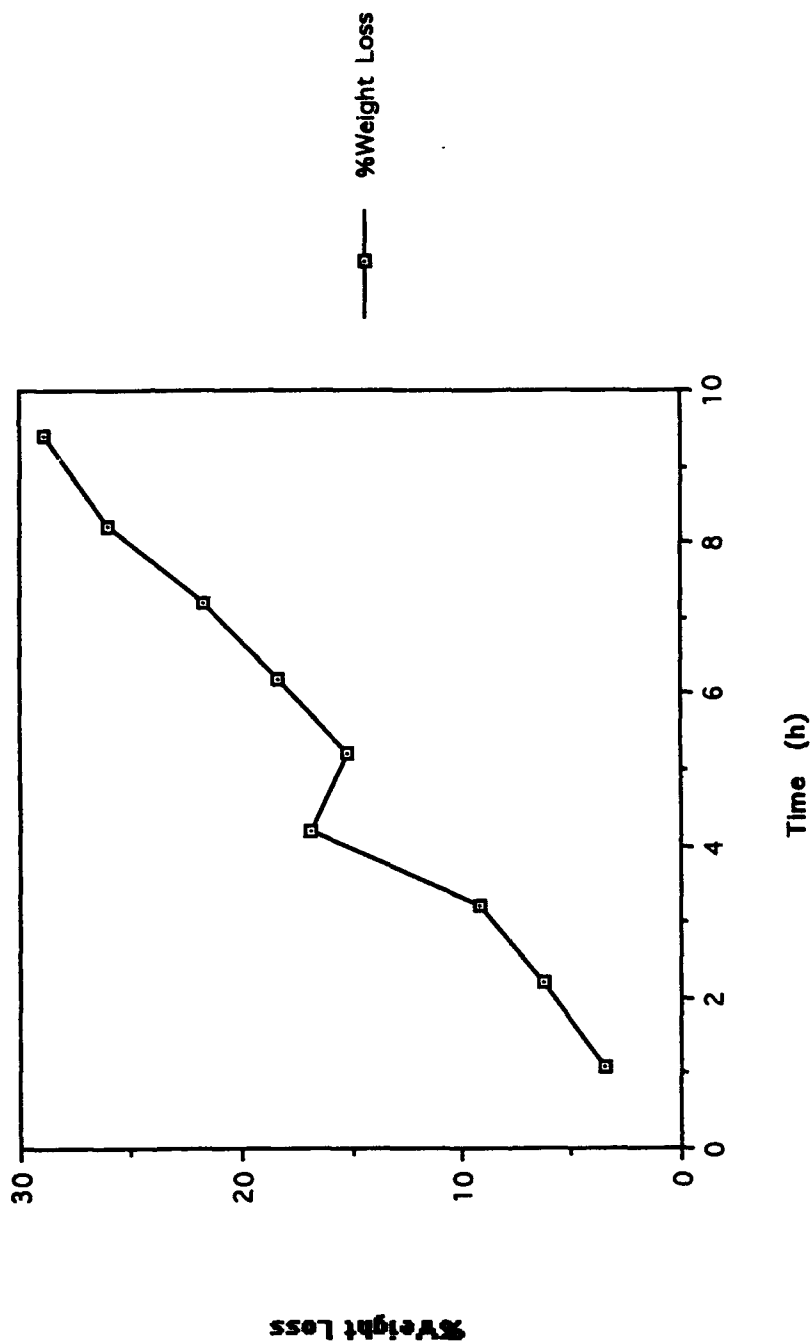


Figure 4: Oxidation Rates of Triple Coated T300 Blocks

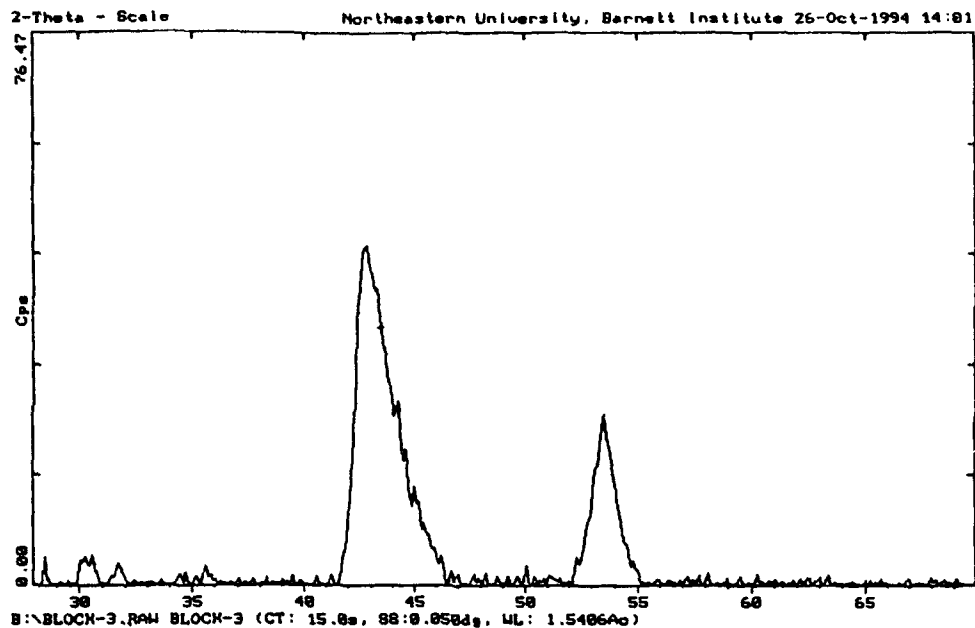


Figure 5: X-ray Powder Diffraction Pattern of Residue From Complete Pyrolysis Of A T300 Block Coated With "HfAlC₂"

The fate of the aluminum present initially in the coating remains undetermined, although it is possible that the diffraction pattern in Figure 5 contains a mixture of Al₄C₃, Al₂O₃ and HfO₂ (Table 4).

Table 4: X-ray Powder Diffraction Data For Completely Oxidized T300 Blocks Coated With "HfAlC₂"

2-THETA	INTENSITY	R-INTENSITY	
28.439	4	8.69565217	HfO ₂
30.194	5	10.8695652	
30.632	4	8.69565217	
31.656	3	6.52173913	HfO ₂ , Al ₄ C ₃
34.435	1	2.17391304	"
34.654	1	2.17391304	"
35.532	3	6.52173913	"
42.844	46	100	C
43.283	41	89.1304348	C, Al ₂ O ₃
44.234	24	52.173913	C
44.399	17	36.9565217	
44.965	12	26.0869565	HfO ₂
50.083	3	6.52173913	HfO ₂
53.52	23	50	Al ₂ O ₃

Conclusions

The present study on the development of novel organometallic reagents for chemical vapor deposition of early transition metal and aluminum containing materials for oxidation protection of carbon substrates leads to the following conclusions:

1. Alkyl exchange between volatile alkyl group IVB transition metals and aluminum alkyls does not occur
2. Alkyl for hydride exchange between volatile alkyl group IVB transition metals and $\text{AlH}_3\cdot\text{NMe}_3$ is rapid
3. Pyrolysis of mixtures $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and $\text{AlH}_3\cdot\text{NMe}_3$ yields ternary metal carbide products analyzing for " HfAlC_2 "
4. The material obtained from solution coating $\text{Hf}(\text{CH}_2\text{SiMe}_3)_4$ and $\text{AlH}_3\cdot\text{NMe}_3$ mixtures onto carbon blocks followed by annealing under argon provides a measure of oxidation protection for the underlying substrate for short time periods at temperatures in the vicinity of 600°C .